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# Thermal stability and crystallization behavior of $TiO_2$ doped ZBLAN glasses

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ABSTRACT

ZBLAN glasses with the composition (in mol%) of $(100-x)(53\,ZrF_4+19\,BaF_2+5LaF_3+3AlF_3+20NaF)+xTiO_2$ ($x=0$, 1.0 and 2.0 mol%) were prepared using a conventional melting technique in dry nitrogen atmosphere. The thermal stability, glass-forming ability, and crystallization kinetics of the ZBLAN system as a function of the $TiO_2$ concentrations were investigated by Differential Scanning Calorimetry (DSC). Also, the crystalline phases were determined by X-ray Diffraction (XRD). Our study indicates that adding $TiO_2$ in a fluoride system improves the thermal parameters of the glass, which is interesting for applications as optical fiber.



## 1. Introduction

Fluorozirconate glasses are potential candidates for optical telecommunication devices because of their low phonon energy and wide optical transmission window, ranging from the UV to the mid-infrared. Rare-earth-doped fluoride glasses are desirable materials for up-conversion lasers, optical amplifiers, and display devices [1–5]. The fluorozirconate system, notably the $ZrF_4$-$BaF_2$-$LaF_3$-$AlF_3$-NaF (ZBLAN) glass composition, is one of the most stable against devitrification among the fluoride glasses [6]. However, fluoride glasses have some drawbacks compared to oxide glasses, such as poor chemical and mechanical stabilities. Substantial improvements have been reported in spectroscopic and physical properties of these glasses, either by the combination of oxides with fluorides, or by controlling the crystallization, leading to glass-ceramic systems [7,8].

Glasses containing transition metal oxides have been developed because of their possible applications in memory and switching devices [9]. Although considered a nucleant agent, a small amount of $TiO_2$ in a glass host improves its glass formation ability and chemical durability [10]. The systems containing $TiO_2$ allowed the development of non-linear optical materials [11–14] and high-power solid-state lasers [15]. In order to find a new glass composition with potential for technological development, it is necessary to investigate the thermal stability and crystallization kinetics of the system.

In the present study, the thermal stability, glass-forming ability, and crystallization kinetics of the ZBLAN system doped with different concentrations of $TiO_2$ were investigated by Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD).

## 2. Experimental

ZBLAN glasses doped with $TiO_2$ were synthesized using a traditional method of melting and cooling. High-purity (99.9%) reagents were used: the $ZrF_4$, $BaF_2$, $LaF_3$, $AlF_3$, and NaF were from Fluortran (BDH-Merck), and the $TiO_2$ was from Sigma-Aldrich. The glass compositions synthesized were $(100-x)(53ZrF_4+19BaF_2+5LaF_3+3AlF_3+20NaF)+xTiO_2$ ($x=0$, 1.0 and 2.0 mol%). The batches of 6 g were melted at 1123 K for 30 min in a platinum crucible and annealed for 30 min in a stainless-steel mold heated at 541 K, in a dry nitrogen atmosphere. The samples were made two times.

The characteristic temperatures $T_g$ (glass transition temperature), $T_x$ (onset crystallization temperature) and $T_p$ (crystallization peak temperature) were determined from DSC curves obtained in a Shimadzu TA-50 thermoanalyzer. The samples contained about 6 mg with the particle size in the range of 425–500 μm. To investigate the crystallization kinetics, several heating rates were used during the DSC measurements (2.5, 5.0, 10.0, and 20.0 K/min).

The X-ray Diffractometry (XRD) technique was applied to investigate the creation of crystalline phases after the samples were heated at two different temperatures, $T_x$ and $T_p$. The powder diffraction patterns were acquired in a Rigaku-Rotaflex RINT2000 diffractometer using the CuKα line. The Inorganic Crystal Structure Database (ICSD) was used to analyze the diffractograms.

## 3. Results

Fig. 1 shows the DSC curve obtained on heating rate of 10 K/min for the ZBLAN glass with 2.0 mol% of $TiO_2$, from 500 to 750 K, approximately. The characteristic temperatures $T_g=544$ K, $T_x=647$ K, $T_p=662$ K, and $T_m=713$ K for this glass were obtained as indicated in the figure. This same procedure was also used to find

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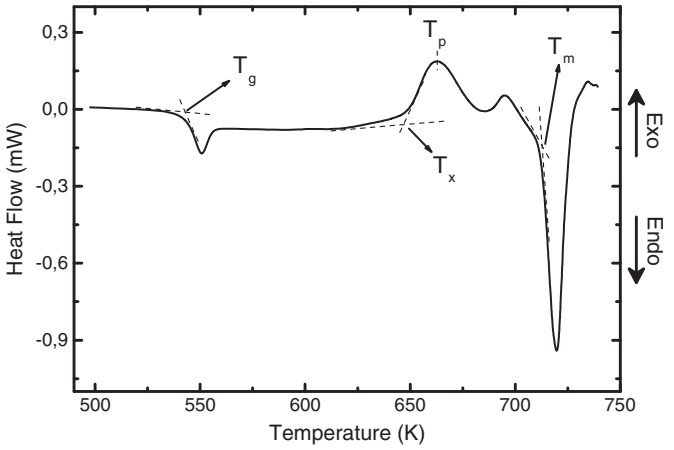


**Fig. 1.** DSC curve for 2.0 mol% of $TiO_2$-doped ZBLAN glass with heating rate of 10 K/min.

these temperatures for the other samples, and the results are summarized in Table 1. Addition of $TiO_2$ to the ZBLAN glass until 2.0 mol% resulted in increases of the $T_g$, $T_x$, and $T_p$ by approximately 1, 7, and 7%, respectively.

The glass forming ability of these glasses was evaluated by three different models proposed by different authors: Dietzel [16], who wrote this parameter as $\Delta T = (T_x - T_g)$; Saad and Poulain [17], $S = (T_x - T_g)(T_p - T_x)/(T_g)$; and the Hruby parameter, $K_H = (T_x - T_g)/(T_m - T_x)$, which predicts that glasses with $K_H \geq 0.5$ will show a greater tendency for glass formation and thermal stability [18]. The values obtained are also shown in Table 1 for the glasses studied. From the undoped sample to the 2.0 mol% of $TiO_2$-doped ZBLAN glass $\Delta T$ and $S$ increase twice while $K_H$ increases 3 times.

In order to determine the crystallization phases of the $TiO_2$-doped ZBLAN glasses, the samples were heated at two different temperatures, $T_x$ and $T_p$. Firstly, the sample temperature was increased in a rate of 10 K/min until $T_x$, staying in the high temperature by 30 min. After that, the temperature was decreased to the room temperature for the X-ray measurements. The same procedure was developed for thermal annealing at $T_p$. The diffractograms were obtained by the X-ray diffraction technique. Fig. 2 shows the diffractograms of undoped (a), 1.0 mol% (b), and 2.0 mol% (c) of $TiO_2$-doped ZBLAN glasses at different thermal annealing. The samples without the thermal treatment did not show any crystalline phases, and of those treated at $T_x$, only the sample with 2.0 mol% of $TiO_2$ showed three crystalline phases: β-$BaZrF_6$, $BaZrF_6$, and $NaZrF_5$. It is important to mention that $T_x$ for 2.0 mol% of $TiO_2$-doped sample is higher than $T_p$ for all samples. At $T_p$, all samples crystallized in five different phases; apart from those crystallized at $T_x$, the phases β-$BaZr_2F_{10}$ and $Na_7Zr_6F_{31}$ could also be observed. The main crystallization phases were β-$BaZrF_6$ and β-$BaZr_2F_{10}$ when the samples were treated at $T_p$, which was expected for the ZBLAN system [19–21]. There was also a transformation from $NaZrF_5$ to $Na_7Zr_6F_{31}$ when the 2.0 mol% $TiO_2$ doped ZBLAN sample was treated at $T_p$.

The crystallization kinetics of these glasses was studied by analyzing the DSC curves for different heating rates, $\phi$. Fig. 3 shows the DSC curves, close to the crystallization peak temperature, obtained for the 2.0 mol% of $TiO_2$ glass, with $\phi = 2.5$, 5, 10, and 20 K/min. The same procedure was also used for the other samples and for all the

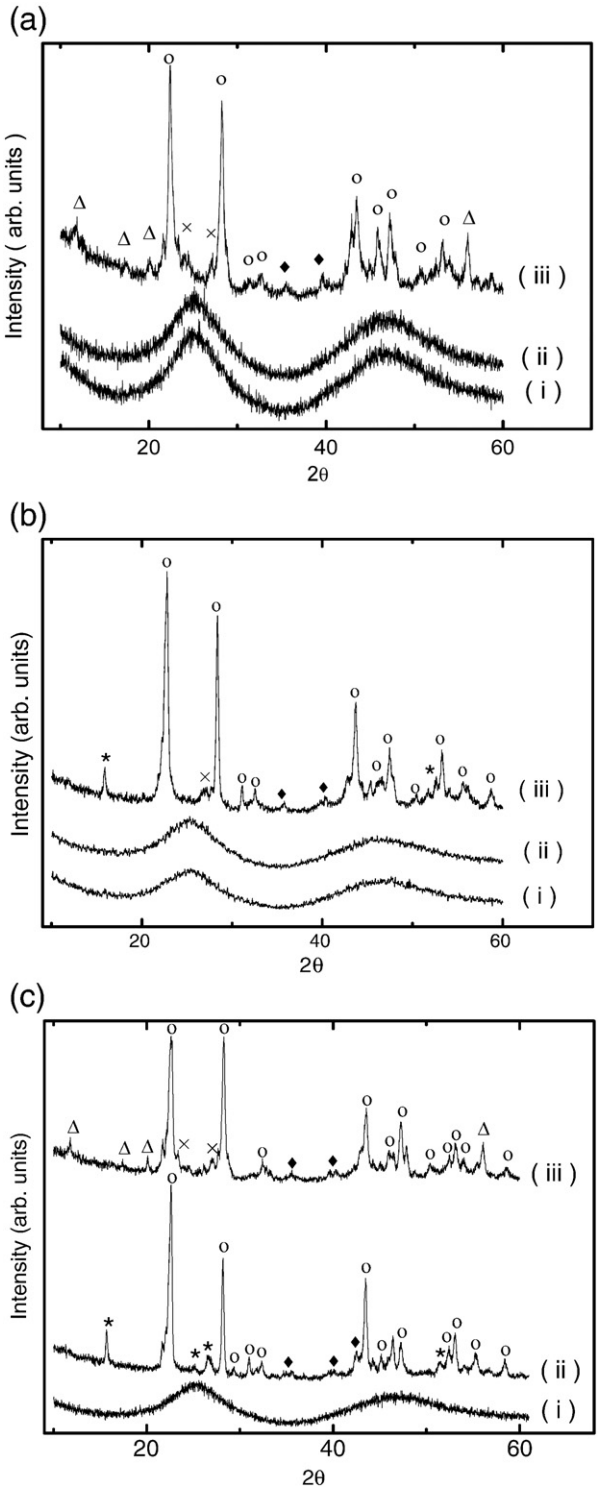


**Fig. 2.** XRD patterns for the ZBLAN (a), 1.0 mol% of $TiO_2$-doped ZBLAN (b) and 2.0 mol% of $TiO_2$-doped ZBLAN (c) glasses. The principal crystallized phases identified were (*) $NaZrF_5$ (Δ) $Na_7Zr_6F_{31}$ (o) β-$BaZrF_6$ (♦) $BaZrF_6$ and (x) β-$BaZr_2F_{10}$. (i) indicates the sample without heat treatment, (ii) after thermal annealing at $T_x$ and (iii) at $T_p$.

**Table 1**
Glass transition ($T_g$), onset crystallization ($T_x$), crystallization peak ($T_p$), and melting ($T_m$) temperatures, measurements by DSC with heating rate of 10 K/min, and the thermal stability parameters $\Delta T$, $S$, and $K_H$ of ZBLAN glasses doped with $TiO_2$.

| ZBLAN: mol% $TiO_2$ | $T_g$ (K) ± 1 | $T_x$ (K) ± 1 | $T_p$ (K) ± 1 | $T_m$ (K) ± 1 | $\Delta T$ (K) ± 2 | $S$ (K) | $K_H$ |
|---|---|---|---|---|---|---|---|
| 0 | 539 | 603 | 618 | 716 | 64 | 1.8 ± 0.2 | 0.56 ± 0.03 |
| 1.0 | 537 | 606 | 623 | 703 | 69 | 2.2 ± 0.1 | 0.71 ± 0.04 |
| 2.0 | 544 | 647 | 662 | 713 | 103 | 2.8 ± 0.1 | 1.56 ± 0.07 |

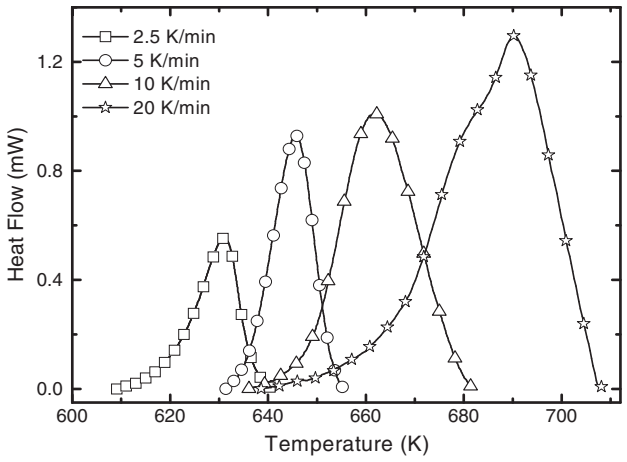


**Fig. 3.** Crystallization peak displacements for different heating rates for the 2.0 mol% of $TiO_2$-ZBLAN glass.

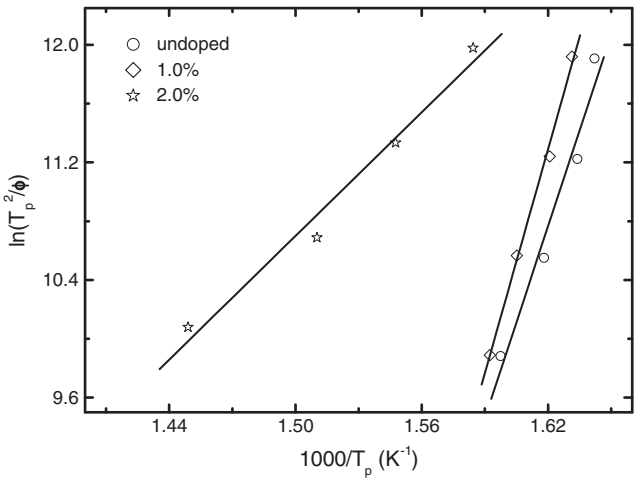


**Fig. 4.** $\ln(T^2_p/\phi)$ vs $1000/T_p$ graph for ZBLAN glasses doped with $TiO_2$. The solid lines are the fits using the Kissinger method to determine the activation energy [27].

peak temperature shifts to high temperature by increasing the heating rates.

## 4. Discussion

The observed increase in $T_g$ with the $TiO_2$ addition corresponds to the viscosity variations. The increase in the super-cooled liquid viscosity with the change in composition refers to the increase in the average strength of the chemical bonds or to the variation in the size of the liquid molecules. An increase in $T_g$ due to the increase in the average strength of chemical bonds was observed in some oxide glasses [22,23]. Moreover, the breaking of weak bonds will occur first during the solid–liquid transition at $T_g$, and when $T_g$ is lower, strong bonds are broken until only molecular units remain [24]. When the $TiO_2$ was incorporated into the fluoride glass matrix, some Ti–F bonds may have replaced the Ti–O bonds, introducing weaker bonds into the matrix. For low concentrations of $TiO_2$, a subtle change in $T_g$ was observed; but at higher concentrations, the increases referred to the higher average bond energy because of the Ti–O covalent bonds, the higher oxygen inclusion induced changes in the low-range structure.

The observed increase in the thermal stability with $TiO_2$ addition can be explained by the confusion principle together with the increase of different chemical compounds [25,26] and also by the crystallization dimensionality. In general, there is a correlation between stability and devitrification during heating, and glass-forming ability. This correlation occurs for glasses that show better glass-forming ability. The sample with 2.0 mol% $TiO_2$ resulted in a better glass composition because it showed greater glass-forming ability and higher stability parameters, as shown in Table 1, such as $\Delta T$, $S$, and $K_H$.

The observed transformation from $NaZrF_5$ to $Na_7Zr_6F_{31}$ when the 2.0 mol% $TiO_2$ doped ZBLAN sample was treated at $T_p$ is due to a metastable state in this system, which is associated with crystal growth during heating [19]. The sample with highest thermal stability (2.0 mol% $TiO_2$) formed three and four crystalline phases simultaneously when treated at $T_x$ and $T_p$, respectively, which did not occur with the less-stable samples (0 and 1.0 mol% $TiO_2$). This tendency towards multiphase formation simultaneously enhances the thermal stability, which confirms our assumption that by increasing the $TiO_2$ concentration in the ZBLAN system, the matrix becomes more thermally stable.

The prediction of low glass-forming ability for the samples with low concentration of $TiO_2$ is in agreement with the difficulties observed during their production. The more-stable glass showed higher crystallization dimensionality due to the fact that nucleation occurred during the thermal heating, above $T_x$, and no during the glass fabrication. Therefore, there is good agreement between the thermal-stability parameters, glass-forming ability, and kinetics parameters.

By the Kissinger model [27], the activation energy $E_a$ under non-isothermal conditions can be written as

$$\ln\left(\frac{T_p^2}{\phi}\right) = \frac{E_a}{RT_p} + \text{constant}, \tag{1}$$

in which $R$ is the Universal Gas Constant. In order to determine $E_a$ for these glasses, the $\ln(T_p^2/\phi)$ vs $1000/T_p$ curves were calculated, and are shown in Fig. 4 for all samples. From the experimental data fit, the activation energy values were determined and are shown in Table 2. The sample with 2.0 mol% of $TiO_2$ showed lower activation energy, which is in agreement with the activation energy paradox for fluoride glasses [24,28]. This behavior was expected, since this glass has high thermal stability.

The crystallization kinetics can be described by the Avrami equation [29–31], in DSC curves, by:

$$x(t) = 1 - \exp(-kt)^n \tag{2}$$

in which $x$ is the crystallization fraction after thermal treatment during time $t$, and $k$ is the transformation rate, which depends on the temperature and includes the nucleation rate and crystal growth rate. The Avrami exponent $n$ is related to the crystal growth mechanisms, and can be uni- ($n=2$), bi- ($n=3$) or tri-dimensional ($n=4$), depending on the transformation mechanisms and nucleation rate. The $k$ values can be evaluated with the Arrhenius equation:

$$k = k_o \exp\left(-\frac{E_a}{RT}\right). \tag{3}$$

Here, $k_o$ is a frequency factor. Eqs. (2) and (3) are the basis for the investigation of crystallization experiments with DSC, but Eq. (2) is strictly applied to isothermal experiments [28,32–34]. The non-isothermal method to study kinetics of transformation based on the

**Table 2**
Activation energy values ($E_a$) obtained by the Kissinger method [27] and the Avrami exponent ($n$) obtained by the Matusita method [35], together with the crystal growth.

| ZBLAN: mol% $TiO_2$ | $E_a$ (kJ/mol) | $N$ | Crystal growth mechanism |
|---|---|---|---|
| 0 | $361 \pm 4$ | 1.9 | Unidimensional |
| 1.0 | $422 \pm 3$ | 1.8 | Unidimensional |
| 2.0 | $117 \pm 3$ | 4.7 | Tri-dimensional |

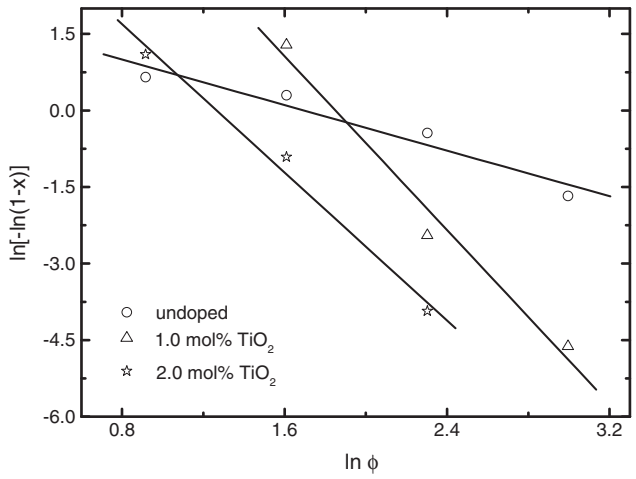


**Fig. 5.** $\ln[-\ln(1-x)]$ vs $\ln\phi$ graph for ZBLAN glasses doped with $TiO_2$. The solid lines are the curve fits obtained by the Matusita method to determine $n$ [35].

process of nucleation volumetric and surface crystallizations was developed by Matusita and Sakka [35]:

$$\ln[-\ln(1-x)] = -n\ln\phi + cte. \quad (4)$$

Here, $n$ is a constant, depending on the crystal growth mechanisms. Fig. 5 shows the experimental data obtained for all samples and the theoretical curves resulting from Eq. (4). From the fit, the Avrami $n$ value could be obtained, and the values are listed in Table 2, together with the crystal growth mechanisms. Considering the crystallization dimensionality as the number of possible routes for devitrification, the undoped and 1.0 mol% of $TiO_2$ doped ZBLAN glasses showed crystallization when heated at $T_x$, due to the saturation of nucleation sites during preparation, and therefore nucleation did not occur during crystallization.

## 5. Conclusions

ZBLAN glasses can accept a small amount of $TiO_2$, with the solubility limit near 2.0 mol%. For high concentrations, the Ti–O covalent bonds in the glass matrix increase, resulting in an increase at $T_g$. The glass sample with 2.0 mol% $TiO_2$ showed lower activation energy, greater crystallization dimensionality, higher thermal stability, and higher glass-forming ability than the glasses with 0 or 1.0 mol% $TiO_2$. Our study indicates that adding $TiO_2$ in a fluoride system improves the thermal parameters of the glass, which is interesting for possible applications.

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